

A general algebraic model for vibrational molecular spectroscopy

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1 Algebraic Model

We present a symmetry-adapted version of the vibron model [1]. The model exploits the isomorphism of the $U(2)$ Lie Algebra and the one dimensional Morse oscillator [4]. A $U(2)$ algebra is assigned to each relevant interatomic interaction. The operators in the model are expressed in terms of the generators of the molecular dynamical group [3], which in the case of triatomic molecules is given by the product

$$U^1(2) \otimes U^2(2) \otimes U^3(2) . \quad (1)$$

A simple realization for those generators is given in terms of angular momentum $\hat{J}_{\nu,i}$ and number \hat{N}_i operators

$$\{\hat{N}_i, \hat{J}_{x,i}, \hat{J}_{y,i}, \hat{J}_{z,i}\}, \quad i = 1, 2, 3 . \quad (2)$$

Instead of working with the generators in Eq. (2) we introduce a new set of generators with well-defined tensorial properties under the point group [2]. The choice of cartesian coordinate system, irreducible representations and Clebsch-Gordan coefficients is given in Ref. [3].

The use of the symmetry-adapted generators allows the connection between the algebraic and the configuration space calculations clarifying the geometrical content of the algebraic approach [2].

The relevant symmetry projected generators for D_{3h} triatomic molecules are

$$\begin{aligned} \hat{T}_{\mu,1}^{A_1} &= \frac{1}{\sqrt{3}} (\hat{J}_{\mu,1} + \hat{J}_{\mu,2} + \hat{J}_{\mu,3}) , \\ \hat{T}_{\mu,1}^E &= \frac{1}{\sqrt{6}} (2\hat{J}_{\mu,1} - \hat{J}_{\mu,2} - \hat{J}_{\mu,3}) , \quad \hat{T}_{\mu,2}^E = \frac{1}{\sqrt{2}} (\hat{J}_{\mu,2} - \hat{J}_{\mu,3}) , \end{aligned} \quad (3)$$

with $\mu = +, -, 0$.

The algebraic Hamiltonian is constructed by repeated couplings of these tensors to a total symmetry A_1 . Terms quadratic in the generators and its products can be expressed in terms of Casimir operators used in former algebraic approaches [4,5]. However, other couplings, which are physically relevant, like \hat{l}^2 written below cannot be expressed in terms of Casimir operators and consequently are not in previous algebraic approaches.

According to this we obtain the Hamiltonian

$$\hat{\mathcal{H}} = \alpha \hat{\mathcal{H}}_{A_1} + \beta \hat{\mathcal{H}}_E + \gamma \hat{\mathcal{V}}_{A_1} + \delta \hat{l}^2 + \alpha^{[2]} \hat{\mathcal{H}}_{A_1}^2 + \beta^{[2]} \hat{\mathcal{H}}_E^2 + \xi^{[2]} \hat{\mathcal{H}}_{A_1 E} + \epsilon (\hat{T}_+^3 + T_-^3) \quad , \quad (4)$$

where

$$\hat{\mathcal{H}}_{\Gamma_x} = \frac{1}{2N_x} \sum_{\gamma} \left(\hat{T}_{-, \gamma}^{\Gamma_x} \hat{T}_{+, \gamma}^{\Gamma_x} + \hat{T}_{+, \gamma}^{\Gamma_x} \hat{T}_{-, \gamma}^{\Gamma_x} \right) \quad , \quad \hat{\mathcal{V}}_{\Gamma_x} = \frac{1}{N_x} \sum_{\gamma} \hat{T}_{0, \gamma}^{\Gamma_x} \hat{T}_{0, \gamma}^{\Gamma_x} \quad , \quad (5)$$

and

$$\begin{aligned} \hat{l} &= -i \sqrt{2} \frac{1}{N_b} [\hat{T}_-^E \times \hat{T}_+^E]^{A_2} \quad , \quad \hat{T}_{\pm} = \hat{T}_1^E \pm i \hat{T}_2^E \quad , \\ \hat{\mathcal{H}}_{A_1 E} &\equiv \frac{(\hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_E + \hat{\mathcal{H}}_E \hat{\mathcal{H}}_{A_1})}{2} \quad . \end{aligned} \quad (6)$$

The Hamiltonian diagonalization and parameter fitting procedures are enhanced using a symmetry-adapted basis [3].

2 Application to H_3^+ , Be_3 and Na_3^+

The three D_{3h} symmetric chosen molecules exhibit a wide range of behaviours, from the very anharmonic spectrum of H_3^+ to the almost harmonic of Na_3^+ .

We present in Table I a least square fit calculation to the *ab initio* calculated vibrational spectrum for these molecules, using an optimal set of parameters of the Hamiltonian. In the H_3^+ case, due to its anharmonicity, we had to include the full set of interactions in Eq. (4) to reproduce the spectrum. The relationship between operators and anharmonicity is clear once the harmonic limit of the AOSM model is explored [2] and the link to configuration space calculations is analyzed.

In addition to the 8 parameters in Eq. (4), the value of the boson number N [4] has to be fixed and it was taken to be $N_{\text{Na}_3^+} = N_{\text{Be}_3} = N_{\text{H}_3^+} = 30$.

This work suggests that the AOSM represents a systematic, simple and accurate alternative to configuration space methods when the integro-differential approach becomes too complex to be applied.

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Table I: Least square energy fit to *ab initio* calculations [6] for Na_3^+ , Be_3 and H_3^+ using Hamiltonian (4). We show the energy differences $\Delta E = E_{abinit} - E_{alg}$. All energies are given in cm^{-1} .

$(v_{A_1} \ v_E^l)$	Γ	Na_3^+ ΔE	Be_3 ΔE	H_3^+ ΔE	
(01^1)	e	0.93	0.51	-1.55	
(10^0)	a_1	1.95	0.02	0.42	
(02^0)	a_1	0.37	-0.74	7.48	
(02^2)	e	0.84	0.17	-5.69	
(11^1)	e	1.68	0.82	-0.61	
(20^0)	a_1	1.26	-0.04	-0.11	
(03^1)	e	-1.19	-2.05	-4.46	
(03^3)	a_1	-0.34	-1.23	3.18	
(03^3)	a_2	-0.33	0.61	2.44	
(12^0)	a_1	-0.01	1.90	0.66	
(12^2)	e	0.34	-1.36	-5.00	
(21^1)	e	-0.19	0.79	4.07	
(30^0)	a_1	-2.06	-1.66	-1.23	
	rms	1.33	1.24	5.84	
Parameters	α	142.40	458.91	3193.60	$\alpha^{[2]}$ -14.86
	β	100.32	396.27	2507.16	$\beta^{[2]}$ -27.75
	γ	21.31	209.74	2807.83	$\xi^{[2]}$ -28.04
	δ	-0.19	-0.95	-13.44	ϵ -0.90

References

- [1] F. Iachello and R.D. Levine, ‘Algebraic Theory of Molecules’, (Oxford University Press, 1995).
- [2] F. Pérez-Bernal, R. Bijker, A. Frank, R. Lemus and J.M. Arias, *Chem. Phys. Lett.* **258**, 301-306 (1996).
- [3] A. Frank, R. Lemus, R. Bijker, F. Pérez-Bernal and J.M. Arias, *Ann. of Phys.* Nov. (1996) In press.
- [4] A. Frank and P. van Isacker, ‘Algebraic Methods in Molecular & Nuclear Structure Physics’, (Wiley Interscience, 1994).
- [5] O.S. Van Roosmalen, I. Benjamin and R.D. Levine *J. Chem. Phys.* **81**, 5986-5997 (1984).
- [6] A.P. Rendell, T.J. Lee and P.R. Taylor, *J. Chem. Phys.* **92**, 7050-7056 (1990).
S. Carter and W. Meyer, *J. Chem. Phys.* **93**, 8902-8914 (1990).